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Palstra, T.T.M.; Nieuwenhuys, G.J.; Vlastuin, R.F.M.; Berg, J. van den; Mydosh, J.A.; Buschow, K.H.J.

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MAGNETIC AND ELECTRICAL PROPERTIES OF SEVERAL EQUIATOMIC TERNARY U-COMPOUNDS

T.T.M. PALSTRA, G.J. NIEUWENHUYS, R.F.M. VLASTUIN, J. van den BERG, J.A. MYDOSH
Kamerlingh Onnes Laboratorium der Rijksuniversiteit Leiden, 2300 RA Leiden, The Netherlands

and

K.H.J. BUSCHOW
Philips Research Laboratories, 5600 JA Eindhoven, The Netherlands

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Magnetisation, specific heat, electrical resistivity, magnetoresistivity and Hall effect were measured for several equiatomic ternary (1-1-1) intermetallic compounds of formula RTX with R = U, Th, Hf and Ti, T a transition metal (Co, Ni, Ru, Rh, Pd, Ir, Pt and Au), and X = Al, Ga, Sn and Sb. These compounds crystallize in three different crystal structures: the cubic MgAgAs-type, and the hexagonal Fe_2P- and $CaIn_2$-types. All U-compounds, which we focus upon in this paper, exhibit magnetic moments of about $3\mu_B/U$ at high temperature and encompass U–U distances from 3.51 to 4.68 Å. For the compounds which the largest U–U distances, Kondo-lattice behaviour was observed. The specific heat coefficient γ shows typical metallic values with some enhancement. Remarkably these compounds have an electrical resistivity up to three orders of magnitude *larger* than that expected and usually found for U-based intermetallic compounds. The Hf- and Th-based compounds serve as nonmagnetic reference materials, however, they also exhibit anomalously larger resistivities.

1. Introduction

The magnetism of U-based compounds has recently attracted great interest especially since the discovery of the strongly interacting heavy-fermion systems. Here novel metallic behaviour was found [1] resulting in large enhancements of the specific heat, magnetisation, resistivity, etc. due to hybridisation of the conduction electrons with the 5f-electrons.

In the present investigation we have fabricated [2] and studied a new series of equiatomic ternary RTX-compounds were R is U, Hf, Th and Ti, T a transition metal, and X a group (III, IV, V) element, e.g. Al, Ga, Sn and Sb. Both local-moment magnetism and Kondo-lattice effects were observed for these compounds, depending on the U–U separation. Interestingly, for the compounds with the highest U–U separation, semiconducting-like behaviour was found in the electrical resistivity, whereas the magnetism shows Kondo-lattice properties and the specific heat indicates a metallic contribution.

2. Experimental procedures and results

2.1. Sample preparation and X-ray diffraction

The samples were prepared by arc melting the constituent elements of at least 99.9% purity under purified argon gas. After arc melting the samples were wrapped in Ta foil and vacuum annealed at 800 °C for 2–3 weeks. The samples were then examined by X-ray diffraction, and it was determined to which one of three crystal structures they belong: the cubic MgAgAs-type and hexagonal $CaIn_2$- and Fe_2P-types.

The compounds (U, Th)NiSn, (U, Th, Hf)RhSb and (U, Th, Hf, Ti)PtSn crystallize in the cubic

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Table 1
Salient properties of the (1-1-1) compounds: structure, nearest actinide separation d, lattice parameters a and c, type of magnetism, Curie and Néel temperatures T_C and T_N, Curie–Weiss temperature Θ_{CW}, effective moment μ_{eff}, saturation moment μ_s, coercive field H_c at 4 K, electrical resistivity ρ at 4 and 300 K and the maximum value ρ the relative resistivity change $\Delta\rho/\rho$ at 4 K and 5 T, linear specific heat coefficient γ and Debye temperature Θ_D

		d (Å)	a (Å)	c (Å)	Magn.	$T_{N,C}$ (K)	Θ_{CW} (K)	μ_{eff} (μ_B)	μ_s (μ_B)	H_c (4 K) (T)	ρ (4 K) ($\mu\Omega$cm)	ρ (300 K) ($\mu\Omega$cm)	ρ_{max} ($\mu\Omega$cm)	$\Delta\rho/\rho$ (10^{-3})	γ $\left(\frac{mJ}{mol\ K^2}\right)$	θ_D (K)
$CaIn_2$	UAuSn	3.60	4.717	7.208	a.f.	35	−4	3.06			650	610	650			
	UPdSb	3.61	4.587	7.215	ferro	65	+70	2.92	0.70	2.40	3500	5300	5300		62	179
	UPdSn	3.65	4.608	7.310	a.f.	29	−10	3.16			430	1500	1500	−82	4.3	–
Fe_2P	UNiAl	3.51	6.733	4.035	a.f.	21	+2	1.70			215	255	255	−6.5	160	
	UNiGa	3.51	6.733	4.022	a.f.	38	+28	2.71	1.30		95	325	325	−620	59	
	ThNiGa	3.67	7.057	4.019	P.p.						32	110	110	+10		
	UCoSn	3.72	7.145	3.994	ferro	85	+25	3.0	1.28	0.38	170	300	300		53	
	ThCoSn	3.84	7.383	4.057	it.ferro	43					47	200	200		3.7	
	URhSn	3.83	7.365	3.993	ferro	25	+8	3.43	1.37	0.02	50	320	320	−13		
	URuSn	3.83	7.345	3.947	ferro	58	+55	2.61	1.13	0.25	120	420	420	+4.2		
	UIrSn	3.84	7.375	4.012	ferro	25	+20	2.86	0.62	0.58	105	295	295			
	URuSn	3.85	7.385	3.915	ferro	35	+30	3.04	0.60	0.58	262	302	302	−28		
MgAgAs	UNiSn	4.51	6.385		Ko	47	−75	3.08			400	1325	7000	−20	28	215
	ThNiSn	4.63	6.544		P.p.						5700	2770	5700		1.5	228
	LaNiSn	(ϵ-TiNiSi)			P.p.						25	360	360		12	198
	URhSb	4.62	6.534		Ko	40	−111	3.25			72000	68000	80000	−27	2.1	214
	ThRhSb	4.71	6.66		P.p.						2640	3000	3000	+3.3		
	HfRhSb	4.41	6.238		P.p.						385	850	850	+8.1		
	UPtSn	4.68	6.617		Ko	~75	−100	3.55			19000	36000	40000	+5.0	11	185
	ThPtSn	4.77	6.749		P.p.						2600	4800	4800	+13	2	–
	HfPtSn	4.46	6.310		P.p.						28000	14500	28000	+2.7	0	
	TiPtSn	4.36	6.16		P.p.						630000	510000	630000	+2.4	0	241

MgAgAs-type structure with F43m space group symmetry (No. 216), where the U-atoms occupy the corners of a regular tetrahedron [2]. The lattice parameters, a, and R–R distances, d, are listed in table 1.

The compounds UPd(Sn, Sb) and UAuSn crystallize in the hexagonal $CaIn_2$-type crystal structure with space group symmetry $P6_3/mmc$ (No. 194), where the U-atoms form trigonal prisms [2]. The lattice parameters a, c and R–R separation $d(=\frac{1}{2}c)$ are also given in table 1.

The third group of compounds crystallizes in the Fe_2P-type crystal structure with space group symmetry P62m (No. 189). This group comprises the compounds UNiAl, (U,Th)NiGa, (U,Th)CoSn, URuSb and U(Ru, Rh, Ir)Sn, and is the one most frequently encountered for equiatomic ternary compounds [2,3]. Here the U-atoms are stacked in layers perpendicular to the c-axis. The lattice parameters and R–R distances are collected in table 1.

2.2. Magnetic properties

The magnetisation was measured using a Foner vibrating sample magnetometer operating at a frequency of 21 Hz. The temperature could be varied stepwise between 1.6 and 300 K and was measured with a calibrated carbon–glass thermometer. A magnetic field up to 5 T could be applied by means of a superconducting solenoid.

The magnetic properties are closely correlated to the different crystal structures and will thus be separated into three groups. As Hf and Th do not carry a magnetic moment, these compounds will be left out of consideration here, and only the U- and Co-based compounds will be discussed. All the MgAgAs-type compounds (UNiSn, URhSb and UPtSn) are magnetic. The high-temperature susceptibility measurements yield effective moments of 3.08, 3.25 and $3.55\mu_B$/f.u. (f.u. is a formula unit of U) and Curie–Weiss temperatures of -75, -111 and -100 K for UNiSn, URhSb and UPtSn, respectively [1]. In spite of these large antiferromagnetic interactions at high temperature, no clear indications of antiferromagnetic ordering are observed at low temperatures. UNiSn has a change of slope in the M–T curve, URhSb a broad maximum at 40 K, and UPtSn only shows a leveling off of the Curie–Weiss increase of the magnetic susceptibility below about 75 K. These effects are illustrated in fig. 1. The two small step-like anomalies in the M–T curve of UPtSn at about 25 and 5 K probably can be ascribed to the presence of $\approx 0.3\%$ of the binary compound UPt, which is ferromagnetic ($T_c = 27$ K) and has a saturation magnetic moment of $0.4\mu_B$/f.u. [4]. Such an impurity phase would explain why the magnitudes of the step-like anomalies are independent of the applied magnetic field and why the ac susceptibility diverges at ≈ 25 and ≈ 5 K. The magnetic isotherms (M–H) show a nearly linear increase of the magnetisation in magnetic fields up to 5 T for all three compounds.

On the other hand for the $CaIn_2$-type compounds, UPdSb orders ferromagnetically, and UPdSn and UAuSn antiferromagnetically. The magnetisation curves (M–T) are shown in figs. 1 and 2. UPdSb has its Curie temperature at 65 K and a remanent magnetisation of $0.65\mu_B$/f.u. The magnetisation loop at 1.57 K exhibits very sharp transitions at the coercive field $H_c = \pm 3.6$ T (see inset fig. 2). The shape of the initial-magnetisation

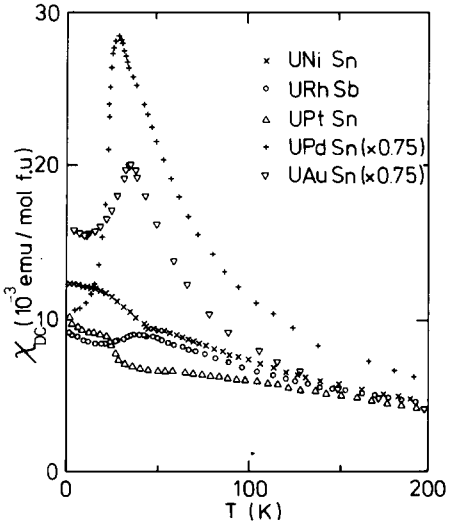

Fig. 1. Temperature dependence of the dc susceptibility of the U-based compound with the MgAgAs-type crystal structure: UNiSn, URhSb and UPtSn and with the $CaIn_2$-type crystal structure: UPdSn and UAuSn.

curve is indicative of narrow domain-wall ferromagnets. Such a general behaviour may be expected for compounds in which the anisotropy energy is larger than the exchange energy. UPdSn and UAuSn order antiferromagnetically at 29 and 35 K, respectively. Furthermore, UPdSn exhibits a spin-flip transition in 4 T at 1.58 K, which is not completed at our maximum available magnetic field of 5 T.

The U-based compounds with the Fe_2P-type structure all order ferromagnetically except for the antiferromagnet UNiAl. Examples of the magnetisation curve for several compounds are shown in fig. 3. The Curie temperatures T_c vary from 25 K for URhSn and UIrSn to 85 K for UCoSn. The values of T_c are given in table 1, together with the corresponding Curie–Weiss temperatures, saturation magnetisation, coercive fields and effective moments. There is no obvious relation between the lattice parameters and the parameters describing the ferromagnetic state. All ferromagnetic compounds exhibit standard ferromagnetic hysteresis loops (M vs. H). For UCoSn it is not clear whether Co also carries a (small) magnetic moment, since the value of the effective moment ($3.0\mu_B$/f.u.) is comparable to the values of the U-moment of the other compounds. A small Co moment might explain why the value of T_c for UCoSn is relatively large in this series of compounds. In this respect it is interesting to note that the related compound ThCoSn exhibits very weak magnetism. A moment value of only $1.4 \times 10^{-2}\mu_B$/f.u. can be induced with 5 T at 4 K. Furthermore it is not clear whether ThCoSn exhibits an (itinerant) ferromagnetic ordering, since an Arrot-plott analysis (see fig. 4) yields straight lines which would indicate a magnetic ordering to occur at 43 K. However, the straight lines are only observed at high magnetic fields where the free-energy expansion, which is the basis of this

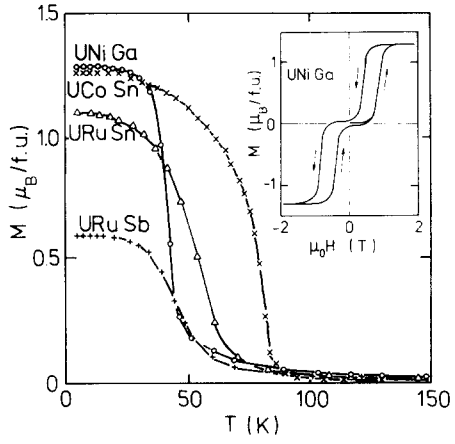

Fig. 3. Temperature dependence of the magnetisation of several Fe_2P-type compounds measured in various magnetic fields: UNiGa in 2T, UCoSn in 0.2 T and URu(Sn, Sb) in 1 T. The inset shows a "wasp-tailed" magnetisation loop for UNiGa at 4.2 K.

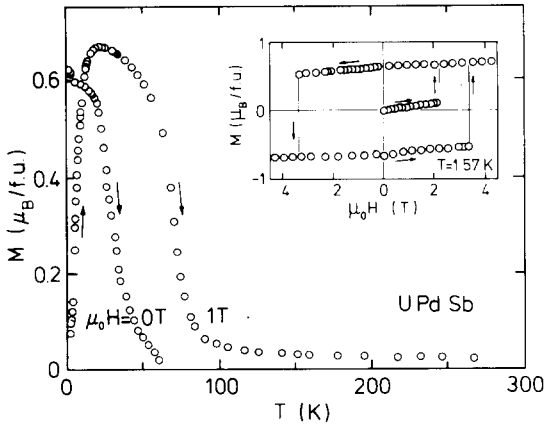

Fig. 2. Temperature dependence of the magnetisation in a field of 1 T and the remanence of UPdSb. The inset shows a rectangular hysteresis loop at 1.57 K.

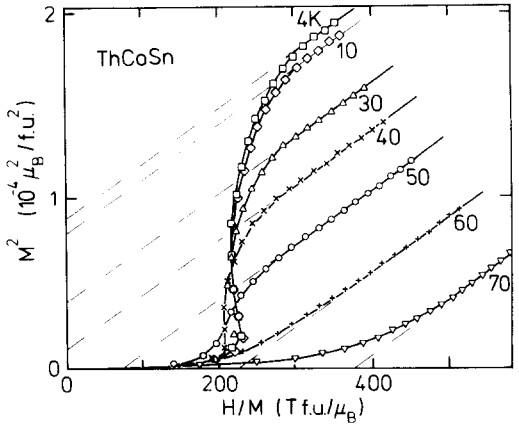

Fig. 4. Arrot-plot (M^2 vs. H/M) for ThCoSn.

analysis, is no longer valid [5]. The negative slope of M^2 vs. H/M points to the presence of a metamagnetic transition at low temperature. Such observations are reminescent of an induced-type of ferromagnetic ordering. The compound UNiGa shows a constricted magnetisation loop (see inset fig. 3). Since no constricted hysteresis loop was found for a single-crystal sample of this compound [6], the constricted loop observed in polycrystalline material may be related to the presence of many grain boundaries, which can act as nucleation centers for Bloch walls and lead to the observed behaviour. UNiAl is the only antiferromagnet with the Fe_2P-type structure. For UNiAl the magnetisation increases linearly with magnetic field up to 5 T.

2.3. Specific heat

We have studied the specific heat of several compounds to obtain information about their electronic properties, e.g. density of states. The specific heat was measured with an adiabatic heat pulse technique. The sample was mounted with apiezon N grease on a thin sapphire substrate. A NiCr heater was vapour-evaporated on this substrate and a non-encapsulated Ge resistor was used as thermometer. The specific heat C was fitted to the formula $C/T = \gamma T + \alpha T^2$, from which the electronic term $\gamma(\sim N(E_F))$ and the Debye temperature θ_D were calculated. These values are listed in table 1. The γ-values vary from 2 mJ/mol K^2 (URhSb) up to 52 mJ/mol K^2 (UPdSb) for the U-based compounds. An even larger value of $\gamma = 160$ mJ/mol K^2 (a "middle weight" heavy-fermion) was reported for UNiAl [7]. The Th-based compounds all have a γ-value of about 2 mJ/mol K^2, while HfPtSn and TiPtSn have a zero value for γ. In the above analysis we have neglected any contributions to the specific heat caused by spin waves in the magnetically ordered state. Such contributions would effectively enhance the measured γ-values listed in table 1 above their true electronic values.

2.4. Electrical resistivity

The electrical resistivity was measured with a standard four point probe technique. A dc current of about 5 mA was used, which could be further reduced in order to avoid self-heating of the samples. The temperature was varied in small steps from room temperature down to 1.4 K, and was measured using calibrated carbon–glass and platinum resistors. The voltages were determined with a Keithley 181 nanovoltmeter. While the relative accuracy of the resistivity is 10^{-5}, its absolute value is only accurate within 2×10^{-2} due to the uncertainties in the determination of the sample dimensions. Possible errors due to macrocracks are eliminated by measuring at room temperature the voltage drop at various distances between the voltage leads using a movable voltage lead mounted on a screw-micrometer. Effects of possible microcracks remain, however, uncorrected. A magnetic field up to 7 T could be applied with a superconducting solenoid, perpendicular to the current direction in the samples.

The electrical resistivity of the MgAgAs-type compounds is shown in figs. 5 and 6. The resistivity is seen to be very high for most compounds and reaches a maximum value of 8×10^4 $\mu\Omega$cm for URhSb at 150 K, which is about three orders of magnitude larger than expected for typical intermetallic compounds [8]. At high temperature

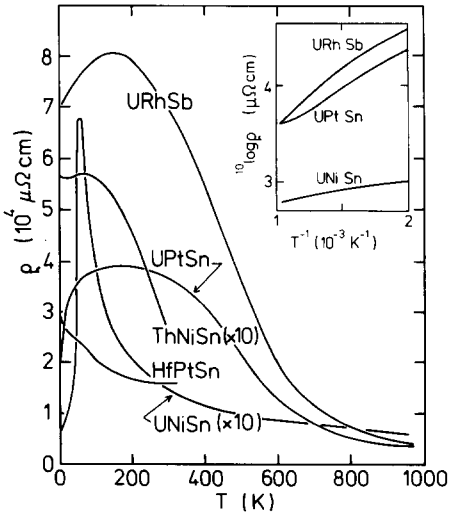

Fig. 5. Temperature dependence of the electrical resistivity of the MgAgAs-type compounds (U, Th)NiSn, (U, Hf)PtSn and URhSb. The inset shows log ρ vs. T^{-1} between 500 and 1000 K.

the resistivity decreases with increasing T. In order to fully investigate the high temperature behaviour, we have extended the measurements for some compounds up to 1000 K. Here an exponential decrease of $\rho(T)$ is observed as is illustrated in the inset of fig. 5. This behaviour is characteristic of semiconductors. By applying the formula appropriate for intrinsic semiconductors: $\rho \sim \exp(E_g/2k_BT)$, we find energy gaps of 0.12 eV for UNiSn, 0.44 eV for URhSb and 0.34 eV for UPtSn. However, such behaviour not only manifests itself for the U-based compounds, but is also observed for the Th and Hf-based compounds, as is clearly illustrated by the $\rho(T)$ plots for ThNiSn and HfPtSn in fig. 5. Below room temperature there are substantial deviations from the exponential behaviour, which can be ascribed to extrinsic or impurity semiconducting behaviour. For comparison, the $\rho(T)$-dependence of LaNiSn (see fig. 6) may be taken as an example of normal metallic behaviour, although this compound has a different crystal structure (ϵ = TiNiSi) [9]. The maximum in resistivity of UNiSn at 55 K does not coincide with the anomaly in the magnetisation, but is ≈ 8 K higher. Furthermore the compounds URhSb and UPtSn do not exhibit any pronounced anomaly of magnetic origin in their electrical resistivity.

The $CaIn_2$-type-structure compounds also have large resistivities. The $\rho(T)$ results are shown in fig. 7. A change of slope in the resistivity occurs at temperatures close to the magnetic phase transitions of UPdSb and UPdSn. The resistivity of UPdSb might be overestimated because the enormous brittleness of the sample and the suspected existence of microcracks. Yet from the large magnitude of the resistivity of UPdSn and from the decrease with the temperature of the resistivity of UAuSn, one might suspect that a semiconducting energy gap is also present in these compounds at high temperatures.

The compounds with the Fe_2P-type structure have high resistivities, up to 430 μΩcm, but they do not exceed the limits of metallic behaviour. The ferromagnetic transitions can be clearly discerned by the change of slope in the resistivities (see figs. 8 and 9). For two of the U-compounds, viz. UNiGa and UCoSn, the contributions of the nonmagnetic scattering processes can be deduced from the behaviour of the corresponding Th-compounds. The compound URuSb deviates from all other ferromagnetic compounds by having a negative temperature coefficient of $\rho(T)$ below T_c. The resistivity of the antiferromagnet UNiAl has a maximum just below T_N(= 21 K) and is still decreasing strongly at 2 K.

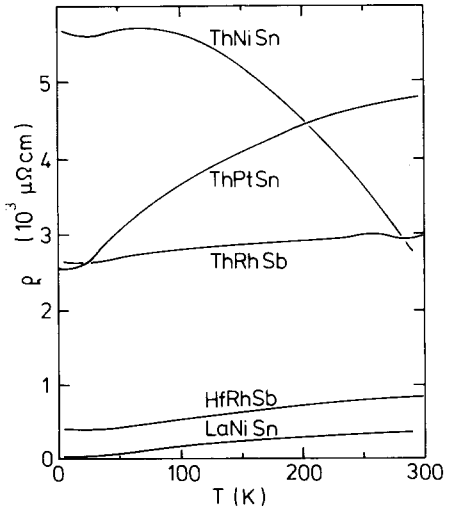

Fig. 6. Temperature dependence of the electrical resistivity of the MgAgAs-type compounds (La, Th)NiSn, (Hf, Th)RhSb and ThPtSn.

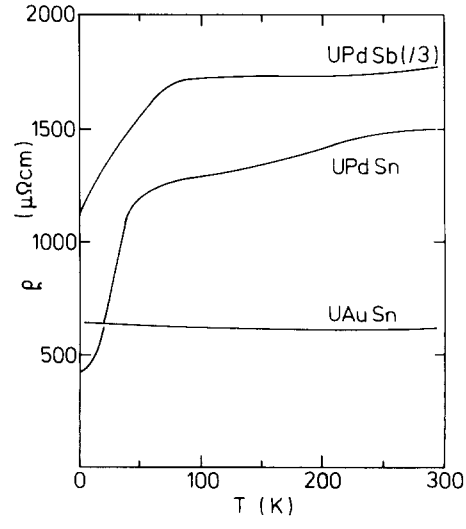

Fig. 7. Temperature dependence of the electrical resistivity of the $CaIn_2$-type compounds UPdSn, UPdSb and UAuSn.

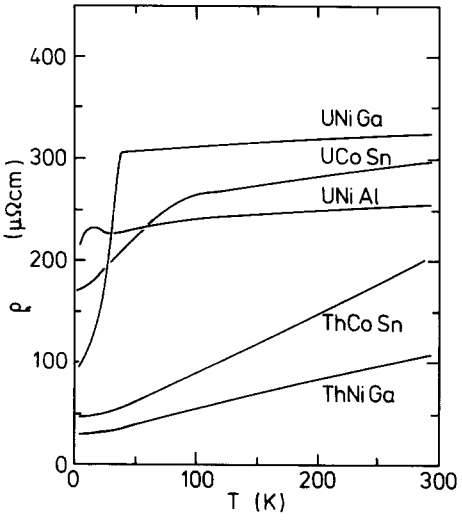

Fig. 8. Temperature dependence of the electrical resistivity of the Fe_2P-type compounds (U, Th)NiGa, (U, Th)CoSn and UNiAl.

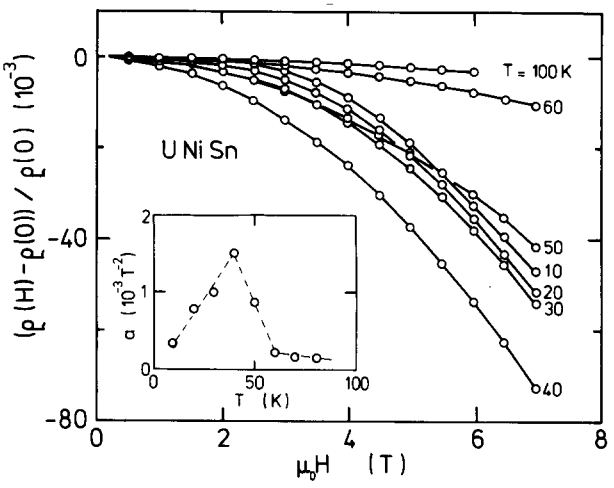

Fig. 10. Magnetic field dependence of the resistivity change $\Delta\rho/\rho$ for UNiSn. The inset shows the temperature dependence of the magnetoresistance coefficient, $a(T)$ (see text).

2.5. Magnetoresistivity

The magnetoresistance of several compounds was measured at fixed temperatures between 4 and 100 K in fields up to 7 T. In figs. 10 and 11 we plotted the relative resistivity change observed in UNiSn and UPtSn, which both have the MgAgAs-type structure. UNiSn has a negative magnetoresistance at all temperatures, which varies almost quadratically with the magnetic field. This H^2-dependence is especially accurate up to 7 T for temperatures above 40 K. Therefore, we show in the inset of fig. 10 the temperature dependence of the coefficient $a(T)$ defined as $\rho - \rho_0 = -a(T)H^2$. We observe a maximum in the magnetoresistivity coefficient $a(T)$ at about 40 K. At

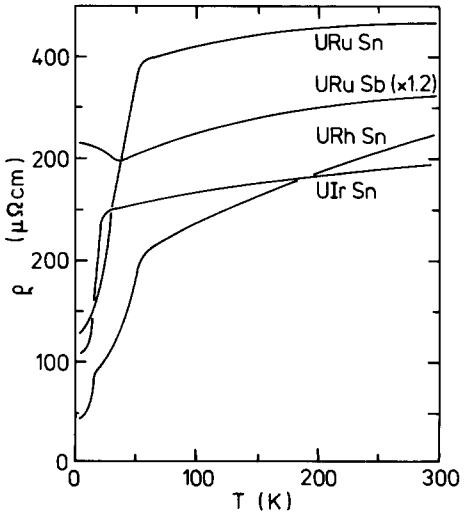

Fig. 9. Temperature dependence of the electrical resistivity of the Fe_2P-type compounds U(Ru, Rh, Ir)Sn and URuSb.

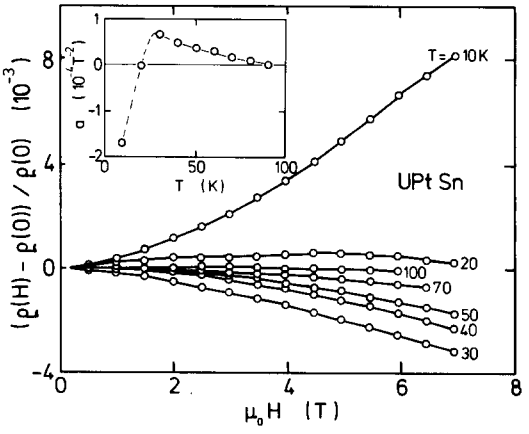

Fig. 11. Magnetic field dependence of the resistivity change $\Delta\rho/\rho$ for UPtSn. The inset shows the temperature dependence of the magnetoresistance coefficient, $a(T)$ (see text).

this temperature there also is a sharp maximum in the resistivity and an anomaly in the magnetisation. Above this temperature the magnetoresistivity decreases rapidly. For UPtSn we observe a positive magnetoresistivity at low temperature, which turns negative for $T > 20$ K. The inset of fig. 11 shows the temperature dependence of the magnetoresistivity coefficient $a(T)$ for UPtSn which has a maximum about $T \approx 30$ K.

For URhSb a negative magnetoresistance was observed at all temperatures. At $T = 10$ K and $\mu_0 H = 7$ T, we found $\Delta\rho/\rho = -0.03$ which then rapidly decreased as $T \rightarrow 30$ K. Above 30 K and in fields up to 7 T the relative resistivity change is less than 5×10^{-3}. ThPtSn exhibits a positive magnetoresistivity and nicely obeys the quadratic field dependence in the entire temperature regime from 4 to 100 K. The coefficient $a(T)$ varies linearly with temperature from -7×10^{-4} T^{-2} for $T = 0$ to 0 for $T = 100$ K. The remaining compounds in the MgAgAs structure have a magnetoresistivity which may be characterized by the $\Delta\rho/\rho$ values at 4 K and 5 T which are listed in table 1.

Values of $\Delta\rho/\rho$ at 4 K and 5 T observed for the compounds with a hexagonal structure are also included in table 1. It is worth mentioning that UNiGa has a resistivity decrease of 60% at 1.4 T. At higher fields the resistivity changes are much smaller. This enormous resistivity change may be related to the strongly field dependent magnetic domain structure expected for this material.

2.6 Hall resistivity

The Hall resistivity was determined with the same equipment as the above (magneto)resistivity by simple adjusting the position of the voltage contacts on the bar-shaped samples of typical dimension $10 \times 1 \times 1$ mm^3. Three samples, viz. UNiSn, URhSb and UPtSn, were thus measured. For all three samples the Hall voltage increases linearly with magnetic field. From the corresponding slopes we can derive values for the Hall angle dV/dH. In URhSb some low-field deviations were observed below 30 K. In this compound the slope was therefore derived from measurements made in higher fields (between 2 and 5 T) where the linear behaviour was manifest. From these slopes we calculated the electron density, $n = -(ec\,dV/dH)^{-1}$. In all three samples the dominant carriers appear to be holes. In fig. 12 the temperature dependence of the carrier density n is shown. Form this plot it follows that for all three compounds the conduction electron density is at least a factor 100 less than expected for metallic behaviour. For instance, if one assumes 3 conduction electrons per formula unit, and a unit cell of $(6.5 \times 10^{-10}\text{m})^3$ (using the X-ray diffraction lattice parameter), one expects an electron density of 4×10^{28} m^{-3}).

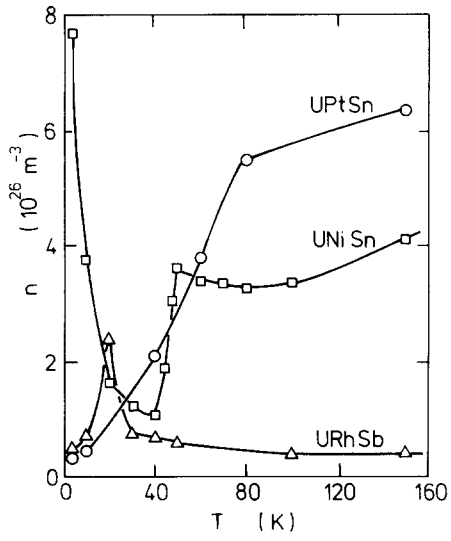

Fig. 12. Temperature dependence of the carrier concentration n for UNiSn, URhSb and UPtSn, as calculated from the Hall resistance measurements.

All three compounds have a rather constant carrier density above 100 K. For UNiSn the increase of the carrier density below 40 K reflects the resistivity decrease in this temperature regime. For URhSb the carrier density remains constant (except for a peak at 20 K) even at low temperature. This agrees with the fact that the resistivity exhibits no pronounced changes. However, for UPtSn the decrease of the resistivity below 50 K is accompanied with a *decrease* in the carrier density.

3. Discussion

3.1. Magnetic properties

The magnetism of the compounds investigated has to be ascribed to the U-moments, as no such large magnetic anisotropies are expected for the other constituent elements in these systems. It has been argued that the U-magnetism is mainly determined by the width of the U 5f-band and only to a lesser extent by its hybridisation with the d- and p-electrons [10,11]. In other words, the U-bandwidth is a measure for the transfer integral between the two spin-bands, which must be sufficiently narrow to support U-moment formation. The U-bandwidth depends critically on the U–U distance. This concept was introduced by Hill, who found a critical U–U separation of about 3.5 Å, below which no magnetism occurred and above which U-moments appeared [12].

In the present investigation all compounds have a U–U separation larger than the Hill-limit, and magnetic moments were accordingly found. However, for the present materials it seems to be rather difficult to find clear trends in the magnetic behaviour, which would enable us to estimate the possible influence of the number of d-electrons of the transition metal element or the influence of the extend that the U–U separation is above the Hill limit. The difficulty of finding such trends may be due to the fact that three different crystal structures are formed. Indeed, the crystal structure has an influence on the magnetic properties because the U–U interaction proceeds via an indirect exchange mechanism, which can be strongly structure dependent. The U–U separation is probably too large for a direct exchange mechanism to be active.

The compounds with the smallest U–U separation are found in the Fe_2P structure, viz., UNiAl and UNiGa. These compounds are very near the Hill limit, which might explain the relatively low values of their effective moments of 1.7 and $2.7\mu_B$/U. The former value is even lower than the smallest moment calculated from Russel–Saunders coupling: $2.54\mu_B$/U for $5f^1$, $3.58\mu_B$/U for $5f^2$, $3.62\mu_B$/U for $5f^3$ and $2.68\mu_B$/U for $5f^4$. Such a small value of the effective moment might indicate a rather broad U-band, which is in keeping with the small U–U separation. By contrast, the specific heat coefficient γ is very large, $\gamma = 160$mJ/mol K^2, from which one expects a high density of states at the Fermi level or, alternatively, a narrow 5f-band. It is not clear at present how to deal with this inconsistency.

The compounds having the largest U–U separation (≈ 4.6 Å) are found in the MgAgAs-type crystal structure, viz., UNiSn, URhSb and UPtSn. The magnetism of these compounds is similar to that observed in the Kondo-lattice systems e.g. $CeAl_3$ and $CeCu_6$ [12]. Namely, at high temperature a large U-moment is found of ($\approx 3\mu_B$/U). The Curie–Weiss temperatures are large and negative (≈ -100 K), indicating large antiferromagnetic interactions. Yet, at lower temperature no definite signs of antiferromagnetic ordering manifest themselves. Instead one observes only weak anomalies. For UNiSn a kink-like anomaly is found at 47 K, for URhSb there is a broad maximum around 39 K, while for UPtSn no intrinsic anomaly is observed but only a "levelling off" of the susceptibility to a constant value. The anomaly of UNiSn at 47 K is probably related to a band structure effect as will be discussed below. Finally, we note that the susceptibility of these three compounds is very large at helium temperature with a value about 100 times larger than the value of Pd. All these features are commonly observed in Kondo-lattice systems. However, there is the remarkable difference between the compounds mentioned above and Kondo-lattice systems, viz. the large resistivity of the former, which implies a greatly reduced number of conduction electrons. This probably means that the magnetic interactions in these compounds are mediated by a superexchange mechanism rather than RKKY interactions.

In addition to the U–U separation, the nonmagnetic elements of the periodic-system of the group III, IV or V also play a role in determining the magnetic properties. Replacement of Sb by Sn in UPdSb preserves the $CaIn_2$ crystal structure and the lattice parameters. But the magnetic order changes from ferro- to antiferromagnetism, the magnetic ordering temperature decreases by a factor of two, and γ decreases by a factor of fifteen.

Likewise, URuSb and URuSn differ in Curie temperature and saturation moment by a factor of two. As a final example we observe that substitution of Ga for Al in UNiAl keeps intact the crystal structure and lattice parameters, but causes an increase of the ordering temperature by a factor of two and a decrease of the γ value by a factor of three. Consequently, the type of magnetism is dependent upon both the s, p-element and the crystal structure. For example Sn favours a ferromagnetic U–U coupling in the Fe_2P structure, but an antiferromagnetic coupling in the $CaIn_2$ structure. Similar conclusions can be drawn for Al, Ga and Sb.

The dependence of the magnetic properties on the number of d-electrons of the transition-metal element is difficult to ascertain, because the crystal structure also varies. For instance, with increasing number of 5d-electrons in going from Ir via Pt to Au, the crystal structure changes from Fe_2P- via MgAgAs- to $CaIn_2$-type for UIrSn, UPtSn and UAuSn, respectively.

In conclusion, we can summarize our experimental findings by stating that the magnetism of the ternary (1-1-1) compounds is dependent on the U–U distance. Local moment magnetism was observed for U–U separations less than 4 Å, while the type of magnetic order was found to critically depend on the crystal structure, the transition metal element (determining also the U–U separation) and the s, p-element. For U–U separations larger than 4.5 Å, the magnetic properties were observed to be similar to those found in Kondo-lattice systems, in spite of the reduced number of conduction electrons.

3.2. Transport properties and specific heat

With regard to the electrical resistivity behaviour of the ternary (1-1-1) intermetallic compounds there is a more clear-cut correlation with the crystal structure than in the case of the magnetic properties. The compounds with the Fe_2P-type structure exhibit normal metallic behaviour. At high temperature the resistivity is dominated by spin disorder scattering (in case of magnetic U-compounds). The mean-free path is of order of the interatomic distances and, therefore,the resistivity cannot increase much further [14]. At the Curie temperature the spin disorder starts to decrease resulting in a change of slope of $\rho(T)$ and a rapid reduction of $\rho(T)$ with decreasing temperature. At helium temperature the spin disorder has vanished for all compounds except for UNiGa. In this case the resistivity can be further reduced, $\approx 60\%$, by applying a magnetic field of 1.4 T. This "disorder" contribution to the resistivity can probably be ascribed to the removal of the dense array of narrow Bloch walls from the sample. Besides the spin-disorder scattering, potential and phonon scattering also contribute to the resistivity, as can be determined from the behaviour of the Th-based compounds.

In contrast to the metallic behaviour of the Fe_2P-type compounds, the MgAgAs-type compounds exhibit semiconducting-like behaviour in the electrical resistivity. Since a semiconducting behaviour is rather unique for ternary intermetallic compounds, we will give particular attention to the discussion on this unusual property. Before doing this we remark that in spite of the rather high measured resistivity of the compounds with the $CaIn_2$-type structure, it is not completely clear whether this property is due to intrinsic semiconducting behaviour or whether it is an experimental artifact caused by distributions of microcracks throughout the samples. In the following we will discuss only the MgAgAs-type compounds.

The semiconducting III–V compounds offer a new and very different type of semiconductor. A basic requirement for semiconductivity is the filled valence band of the anions with 8 electrons, viz., "the ionic criterion for semiconductivity". These anions frequently occupy a face-centered cubic lattice. Then one or two tetrahedral holes, or the octahedral holes, or any combination of these three possibilities of the fcc lattice, can be filled with the cations, leading to five basic combinations [15]. The simplest crystal structure is obtained when filling the octahedral holes, resulting in the NaCl structure. By filling of one of the tetrahedral holes, the ZnS structure results, in which, e.g., GaAs crystallizes. The CaF_2 structure is obtained by filling both tetrahedral holes. When the two different F-sites of the CaF_2 structure are

alternately occupied by different atoms, the MgAgAs structure is obtained. This structure can also be constructed by three interpenetrating fcc lattices, with the anion and the two tetrahedral holes as sublattice origins. For compounds in this crystal structure, semiconducting behaviour was observed when a group-V element occupies the Ca-sites of the CaF_2 structure, e.g. AsAgMg and SbAgMg [15]. Note that these compounds also obey the ionic criterion for semiconductivity. However, metallic behaviour was found when the anion occupies the Ca site, e.g. CuSbMg.

Very recently, band structure calculations have revealed the phenomenon of half-metallic ferromagnetism for a MgAgAs-type compound: NiMnSb [16]. Here it was argued that owing to the loss of inversion symmetry on the Mn-site $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and the large exchange splitting of the Mn d-band, a different interaction exists between the electrons in the majority spin band with respect to the minority spin band. This in turn causes metallic behaviour for the majority band and semiconducting behaviour for the minority band where an energy gap exists at the Fermi level.

We conclude from our resistivity measurements that owing to the absence of exchange splitting for both the U- and nonmagnetic (Th, Hf)-compounds, there are no spin-split bands, even though an energy gap seems to appear around the Fermi-level in the energy spectrum of all electrons. It is not clear what causes the opening of the band gap. The occurrence of the gap for the Hf- and Th-based compounds indicates that it probably results from an interaction of d-electrons with Sb p-electrons, rather than from the 5f-electrons with the Sb p-electrons. Nevertheless, at low temperature deviations from the exponential resistivity behaviour were observed for all MgAgAs-type compounds. These can be ascribed to impurity states, or more likely, to a temperature dependence of the energy gap, probably induced by the magnetic behaviour.

In order to check the existence of a band gap in these materials, we have measured the Hall resistivity of three compounds: UNiSn, URhSb and UPtSn. Assuming there are *only* electrons or holes, the density of carriers was estimated to be at least a factor 100 less than expected for metallic behaviour. This further confirms the presence of a band gap. For UNiSn we observe at low temperature an enormous increase of the carrier density, which explains the decrease in the resistivity. Probably, the narrow band gap of 0.12 eV at high temperature closes at about 50 K, resulting in metallic-like behaviour at helium temperature. For URhSb and UPtSn the resistivity decreases at low temperature with decreasing carrier density. This effect is anomalous but might be related to a decrease of the gap below 100 K, influenced by the magnetic behaviour.

The indication of a band gap is, however, in contradiction with the nonzero values of the linear term in the specific heat, γ, which usually can be taken to be proportional to the density of states at the Fermi surface. For some compounds we found values of γ comparable to that in normal metals inspite of the high resistivities at low temperature. For instance, the compound UPtSn has a residual resistivity of 19000 $\mu\Omega$cm, while we observed $\gamma = 10.9$ mJ/mol K^2 (in Cu $\gamma = 0.7$ mJ/mol K^2). The nonmagnetic compound HfPtSn and TiPtSn have zero γ-values. This suggests that the magnetism plays a definite role here and that the γ-values, as determined from the above analysis, might be unduely influenced by spin waves or other types of magnetic excitations at low temperatures. More study is needed to clarify this unusual situation of a large γ-value in a semiconducting state.

As another possibility we use the XPS-measurements on UNiSn, URhSb and UPtSn that have revealed a narrow 5f-band located just below the Fermi-level [17]. Consequently, the value of γ resulting from the valence electrons could be enormously enhanced by the same type of interactions present in heavy-fermion systems [13]. In this case γ is enhanced by hybridisation of the conduction electrons with the 5f-electrons, the latter filling a very narrow band. This effect must, however, be absent for the Th- and Hf-based compounds, as these compounds have no 5f-electrons. Accordingly, the compounds UPtSn and ThPtSn have γ-values of $\gamma = 11$ and 2 mJ/mol K^2, respectively, whereas UPtSn has a much larger residual resistivity of 19000 $\mu\Omega$cm than ThPtSn with 2600 $\mu\Omega$cm. Thus in spite of a significantly smaller conductivity (by a factor of 7), the value of γ is still a factor

of 5 larger for UPtSn with respect to ThPtSn. Unfortunately, the resolution of the XPS-measurements is not sufficient to reveal the existence of a band gap.

4. Concluding remarks

We have studied the crystallographic, magnetic and electrical transport properties of a number of equiatomic intermetallic compounds RTX, in which R = U, Th or Hf is combined with a transition metal T(Co, Ni, Ru, Rh, Pd, Ir, Pt or Au) and an s, p element X(Al, Ga, Sn, Sb). Most of the U compounds were found to be magnetic, but there is no clear correspondence between the type of magnetic ordering and the crystal structure of the valence electron concentration. By contrast, the structure plays a rather crucial role in determining the electrical transport properties of these materials. Normal metallic conduction is found in hexagonal compounds of the Fe_2P type, whereas an unusual resistivity behaviour, reminiscent of that in semiconductors, is found for compounds crystallizing in the cubic MgAgAs structure. The physical origin of the latter resistivity behaviour is still unclear and our experimental results obtained from (magneto) resistivity specific heat and the Hall effect are often contradictory when it comes to interpret the electrical transport properties in terms of energy gaps present in the band structure of these compounds. The only firm conclusion that can be drawn from a comparative study of the properties of these materials is that the anomalous behaviour of the electrical properties of the MgAgAs compounds is not solely the results of the 5f-electron system. The same experimental properties for new series of nonmagnetic (1-1-1) compounds are presently being investigated and will be the subject of a future publication.

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